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Neutron Activation Analysis for Simultaneous Determination of Trace Elements in Ambient Air Collected on Glass-Fiber Filters

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16. ABSTRACT

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Neutron Activation Analysis for Simultaneous Determination of Trace Elements in Ambient Air Collected on Glass-Fiber Filters

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Arsenic with 25 other elements are simultaneously determined in ambient air samples collected on glass-fiber filter composites at 250 United States sites. The instrumental neutron activation analysis (NAA) technique combined with the power of a dedicated mini-computer resulted in a routine analysis of the collected filter composites. The computer output defined ambient air levels for each element in units of nanograms per cubic meter. Values for the range determined, the mean, and coefficients of variation for split and control samples are reviewed for each of the elements involved in this multielement scan. Thirteen of the 26 elements are detected in concentrations above the discrimination limits in over 20% of the samples analyzed.

Air quality sampling and monitoring has been actively pursued by the National Air Surveillance Network (NASN) since the early 1960's (*1*). This network established stations in urban and nonurban areas to collect air samples using a Hi-Vol sampler (High Volume Air Sampler (Hi-Vol) is specified for the network and is commerically available.) The collected filter samples provide information concerning the present air quality as well as means to study national trends. For the years 1975 and 1976 a section of the collected filter samples was assigned to the NAA program for the study of a specific element, arsenic.

Previous ambient air studies by NAA were performed by Dams et al. (*2*), Rancitelli et al. (*3*), and Zoller et al. (*4*). In these studies a special filter material having low blank values was used. Dams stated that glass-fiber filters must be ruled out for nondestructive activation analysis because they contain high concentrations of trace metals. Dams also required a special hand calculation for arsenic using a minor γ-ray energy peak at 657 keV to avoid any interferences from bromine and antimony at arsenic's major γ-ray energy peak (559 keV).

Since NASN sampling procedures specify glass-fiber filters for sample collection, an NAA method was developed to minimize the effects of high background interferences due to the filter matrix. This NAA method was specifically developed to avoid time-consuming wet chemistry procedures and to utilize an instrumental NAA approach designed to resolve the major arsenic γ-ray energy peak.

This paper describes how using specific irradiation and decay conditions and adapting a simple calculation method to a dedicated mini-computer resulted in the determination of finite arsenic values in the collected samples. Supplementary information gathered simultaneously with the arsenic data was analyzed by the computer program, resulting in an output for additional elements. A subsequent count of the samples after a longer decay period along with the initial analysis resulted in a multielement scan for 26 elements. Early experiments on the first 200 samples determined levels for an additional seven elements. However, the analysis for these additional elements (Al, Cl, Cu, Mg, Mn, Na, and V), which have short half-lives, was discontinued to limit sample handling to that irradiation in which the element arsenic was determined.

To demonstrate the utility of the method for determining the concentration levels for arsenic and 25 other elements in the atmosphere using the NASN samples collected on glass-fiber filters, a group of 400 quarterly filter composites was initially evaluated.

EXPERIMENTAL

Apparatus. A 1-MW Pulstar nuclear reactor at North Carolina State University (NCSU) is used. Average thermal neutron flux during each 4-h irradiation is approximately 10^{13} neutrons/cm^2/s.

Also used is a germanium solid state detector, Ge(Li), with a γ-ray efficiency of 21% and a pulse-height resolution of 2.2% fwhm at 1.332 MeV. The detector is shielded in 5.1 cm of lead. The output of the detector is fed to as pulse-height analyzer, 2048-channel storage memory, which has a gain set for 1 keV per channel of memory. The associated dedicated computer has 32K bits capacity—16K assigned to data. A dual disk system provides one disk for programs and one disk for data storage.

Vials. Polyethylene sample vials, with a capacity of $^2/_5$ dram (0.7084 g), are used to contain samples during irradiation and polyethylene counting vials, with a capacity of 2 drams (3.542 g), are used to transfer samples after irradiation. Polyethylene conical vials, 250 or 400 μL capacity, are used to contain solid and liquid standards during irradiation and counting.

Reagents. Solid standards are NBS SRM #1632 at approximately 200 mg and NBS SRM #1633 at approximately 100 mg. Liquid standards for the elements As, Mo, Cd, Sb, Sn, Ca, Fe, Se, Cr, Ba, Ni, and Zn are microgram levels of Fisher AA solutions. The control sample is NBS SRM #1630 at approximately 200 mg.

Collection. NASN sample collections are used. Hi-Vol filter samples are collected on a 12-day schedule. At each of 250 sites for a 24-h period, approximately 2500 m^3 of air are pulled through a 20 × 25 cm fiber-glass filter medium. These individual samples are then combined by quarters and analyzed to obtain quarterly composite measurements at each site (*5*). A filter bank maintains inventory of these filters which are to be analyzed by different techniques. The quarterly composites are prepared for NAA by filter bank personnel using a 1.9-cm diameter punch on the biweekly samples and then combining these punch-outs into the quarterly composite for each location.

Procedure. After receiving the samples from the filter bank, approximately 39 cm^2 of the punched filter material are placed into two irradiation vials. Each vial is irradiated 4 h using the NCSU Pulstar Facilities. The bottles containing the vials are then allowed to decay in the reactor pool for 6 to 7 days. After removal from the pool, each composite is transferred from its irradiation vial to an appropriate counting vial. At a decay time of 10 days, each composite is counted on the Ge(Li) detector using the pulse-height analyzer. The resulting γ-ray spectrum is then recorded on the data disk. A second count, after at least 16 days decay time, is also recorded on the data disk. Standard, control, and split samples are handled in a like manner. A split sample is a replicate sample, not identifiable to the analyst but known to the filter bank personnel, and therefore processed as a blind sample. A control sample is a specific aliquot (from a known sample) used with every group of samples. The control sample permits a current evaluation of day to day repeatability as well as an on-line evaluation of the equipment being used. Usually

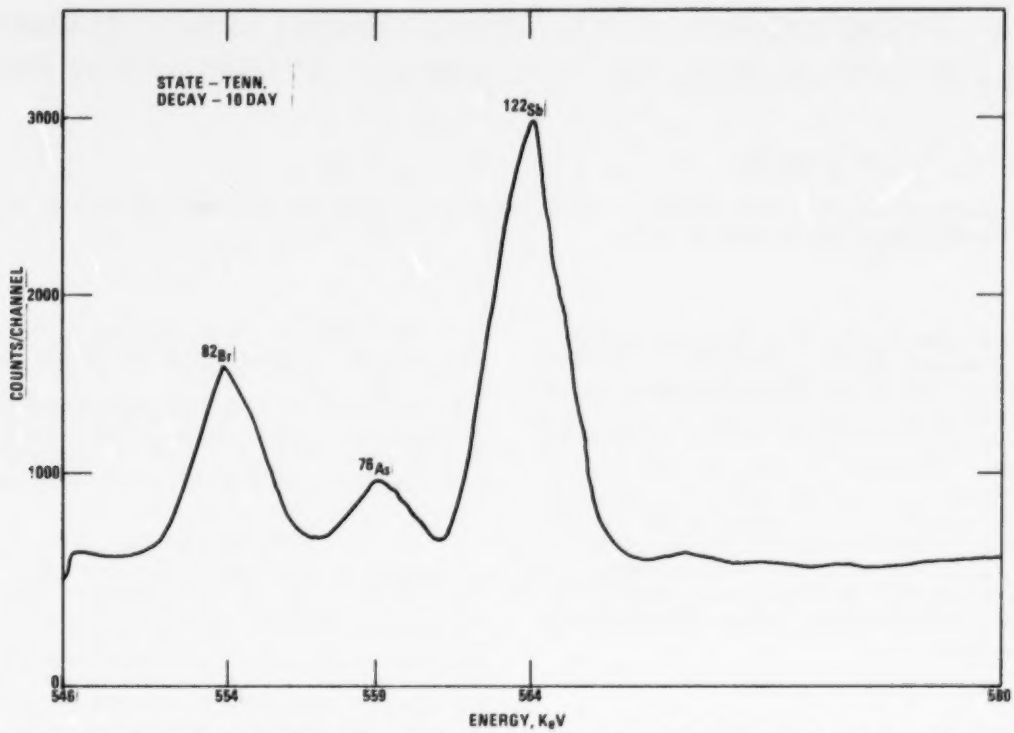

Figure 1. Partial γ-ray spectrum showing the Br, As, and Sb photo peak areas from a filter composite sample after a ten-day decay time

14 filter composites, one control sample, one split sample, and standards are irradiated as a group. Fifty such groups were necessary to handle the NASN composites for one year.

Quantitation. Data reduction occurs as each count is recalled from the data disk file and subjected to a computer analysis. The programmed Covell technique (*6*) results in a gross peak area for each element listed in the computer library. Since the various elements can have several isotopes and/or γ-ray energy peaks, one isotope and one peak area for each element is selected for computer analysis. The radio nuclide, half-life, energy and decay times selected for each element are listed in Table I. Corrections are made to the peak area for decay time, counting time, and unit of measurement. The resulting net peak area is then compared with a similar peak area of the standard to determine the number of nanograms per square inch. This number is multiplied by 63 (total square inches of filter exposed) resulting in the total amount of the element found on the filter. The filter media contribution (filter background) is then subtracted. This result, divided by the volume of air passed through the total filter, is the nanograms of the element per cubic meter of air associated with the air particulates.

If no peak area is determined by the Covell technique, the background area associated with the γ-ray energy of the element is used to give a best estimate of a value at which sample concentration may be less than but will not exceed that value (*7*).

Discrimination Limit. High signal/noise ratios from the glass-fiber filter matrix made it necessary to determine a tolerance interval (*8*) for the lot of filters being used in the sample collection. At the beginning of this effort, a reserve stock of blank filters, similar to those being used in sample collection, was analyzed as routine samples. The mean values obtained from this group of blanks were used to correct the filter composite samples for filter background. The standard deviations of the blank were multiplied by 3.3 and divided by 2500 m^3 of air (an estimated average for a 24-h Hi-Vol air sample) to determine the tolerance interval. For the filter group under analysis, this tolerance interval becomes a method-dependence atmospheric concentration. Any analytical result above this concentration can be ascribed, with relative certainty, to the atmospheric particulate; any results below this concentration cannot be discriminated from filter media contributions (*9*).

Table I. Nuclear Parameters Relating to the Measurements of Specific Elements in Ambient Air

element	nuclide used	half-life	energy used in measurement	decay time
antimony	^{122}Sb	2.75d	564	10d
arsenic	^{76}As	26.3h	559	10d
barium	^{131}Ba	11.3d	496	>16d
bromine	^{82}Br	35.8h	554	10d
cadmium	^{115m}In	2.3d	337	10d
calcium	^{47}Ca	4.7d	1297	10d
cerium	^{141}Ce	32.5d	145	>16d
cesium	^{134}Cs	2.07y	796	>16d
chromium	^{51}Cr	27.8d	320	>16d
cobalt	^{60}Co	5.26y	1173	>16d
europium	^{152}Eu	12.2y	1408	>16d
hafmium	^{181}Hf	45d	482	>16d
iron	^{59}Fe	45d	1099	>16d
lanthanum	^{140}La	40.3h	1596	10d
lutetium	^{177}Lu	6.74d	208	>16d
molybdenum	^{99}Mo	67h	140	10d
nickel	^{58}Co	71d	811	>16d
rubidium	^{86}Rb	18.6d	1078	>16d
samarium	^{153}Sm	47h	103	10d
scandium	^{46}Sc	83.9d	889	>16d
selenium	^{75}Se	120d	264	>16d
tantalum	^{182}Ta	115d	1222	>16d
thorium	^{233}Pa	27d	312	>16d
tin	^{113m}In	115d	392	>16d
ytterbium	^{175}Yb	4.2d	396	10d
zinc	^{65}Zn	245d	1115	>16d

RESULTS AND DISCUSSION

Triplet. Figure 1 is a partial γ-ray energy spectrum for an irradiated Hi-Vol filter composite taken from a city in Tennessee. Note the triple peak area associated with the detection of ^{82}Br, ^{76}As, and ^{122}Sb. In processing the filter blanks, the arsenic detection was optimized with respect to the Br and Sb peak interferences as well as the high back-

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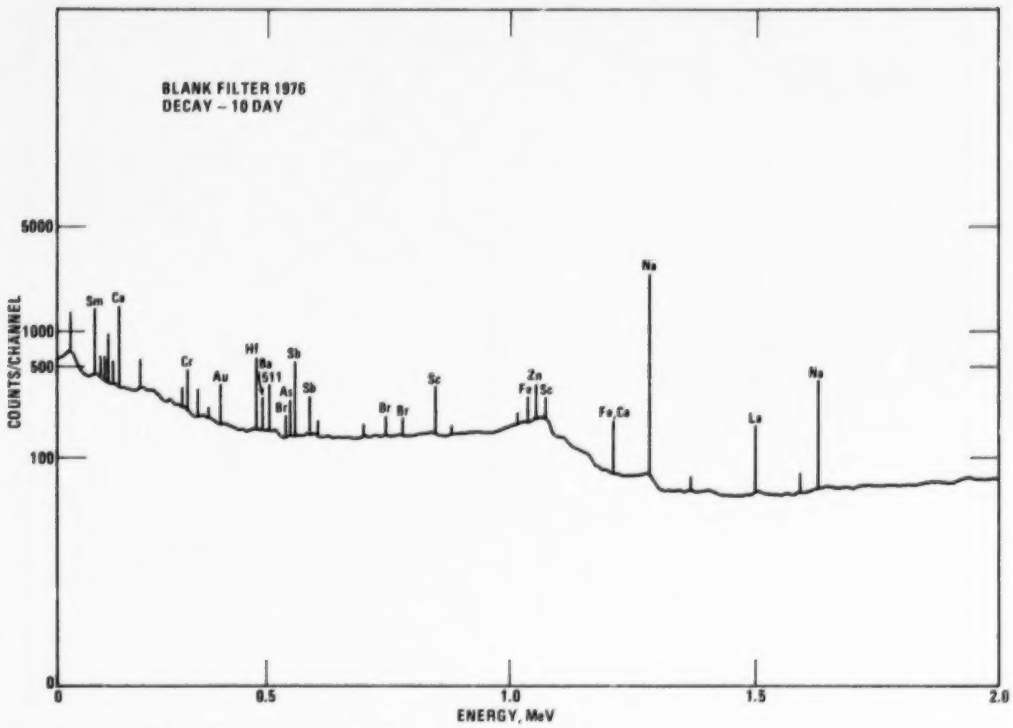

Figure 2. γ-ray spectrum from a blank filter sample after a ten-day decay time

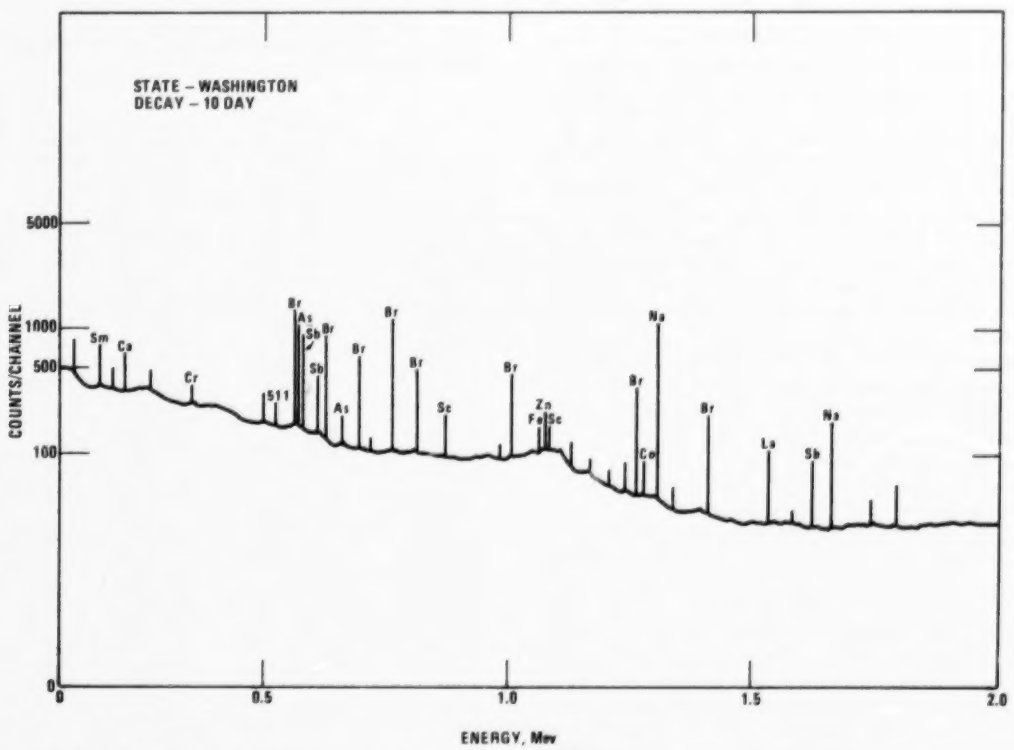

Figure 3. γ-ray spectrum from a filter composite sample after a ten-day decay time

ground contribution from ^{24}Na. This optimization resulted in setting 10 days decay as the counting time which resulted in the best finite values for Br, As, and Sb using the high resolution ability of the Ge(Li) detector. However, in the actual determinations of air samples, 15% of the arsenic peaks were lost due to interferences from ^{82}Br and/or ^{122}Sb (no peak area calculated by the program) along with the large background contribution from ^{24}Na.

Filter Background. Figure 2 is a γ-ray spectrum for an irradiated filter blank. Note that many of the elements appear

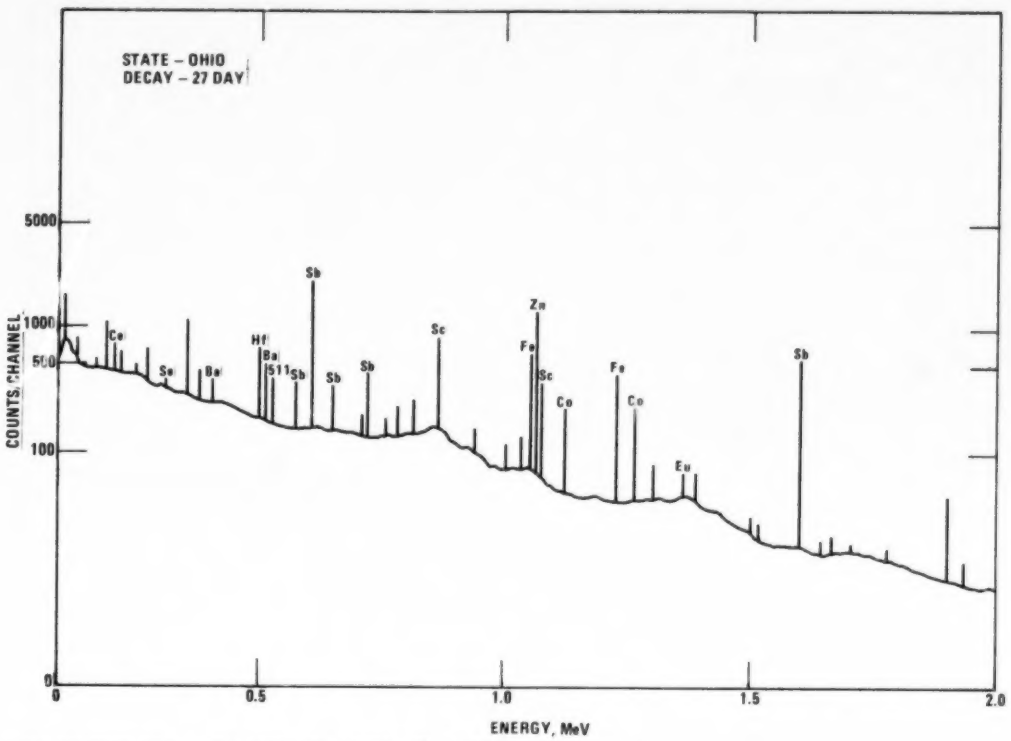

Figure 4. γ-ray spectrum from a filter composite sample after a 27-day decay time

in this spectrum along with the dominate ^{24}Na peaks. By using the dispersion in filter blank values, discrimination limits are computed. These limits are recorded as the first number of the "Range" column of Table II. The discrimination limit for As, in nanograms per cubic meter, is 4. This is comparable to the value reported by Dams (2) showing that the use of the major γ-ray peak of arsenic can compensate for the loss in detection caused by the glass-fiber filter background.

Qualitative. Figures 3 and 4 are γ-ray spectra for an irradiated composite collected from a city in Washington after a decay of 10 days and for an irradiated composite collected from a city in Ohio after a decay of 27 days respectively. Note the still dominate peaks of ^{24}Na in Figure 2 and 3 but the obvious increases of As, Sb, and Br in Figure 3 while in Figure 4, the ^{24}Na peaks have decayed away and well defined peaks for Ce, Hf, Sb, Fe, Zn, Co, and Eu are readily apparent. The ten-day decay count produces data for the elements As, Br, Ca, Cd, La, Mo, Sb, Sm, and Yb; the 27-day decay count produces data for the elements Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, Lu, Ni, Rb, Se, Sc, Sn, Ta, Th, and Zn.

Quantitative. Table II summarizes the data collected from a random group of 400 composite filters. Shown are the expected and actual concentration range and mean for each element analyzed. The last column is the percent above the discrimination limit. This percent is related to the number of composite filters in which a finite concentration of an element is found to be higher than the discrimination limit. Elements with zero % above discrimination are not detected, at this time, using the NAA method. In half of the elements scanned, the percentage above discrimination was over 20%. For the element arsenic, the percentage was 23%.

The Expected Range column is a listing of the lowest and highest concentrations found in References 1–3, and 10. These numbers, derived from several different analytical methods, are useful in comparing the reported concentration ranges with some other available values. The listing of these numbers does not indicate acceptance of the validity of the data but is useful for a general comparison. The two range columns produce reasonably comparable results for the elements of Sb, As, Br, Cs, Cr, Co, Fe, La, Rb, and Sc. The remaining elements are restricted by the lack of method sensitivity, high discrimination limits caused by the filter background, or a general lack

Table II. Results from NAA Application to Glass-Fiber Filter Composites

element	expected range,[a] ng/m³	range,[b] ng/m³	mean, ng/m³	% above discrimination, %
antimony	1–200	0.7–133	4.1	61
arsenic	4–90	4–183	15	23
barium	50–200	3000 (DL)	---	0
bromine	6–1000	3–717	121	93
cadmium	0.4–90	3–36	7	18
calcium	800–30000	13000 (DL)	---	7
cerium	0.3–30	1.8–78	4.3	76
cesium	0.3–5	0.3–1.6	0.4	11
chromium	3–400	7–124	17	26
cobalt	0.2–30	0.3–3.7	1.0	98
europium	0.03–1	0.2 (DL)	---	0
hafnium	0.05–5	1.2 (DL)	---	3
iron	500–25000	900–4900	1540	50
lanthanum	1–30	0.7–8.7	1.9	78
lutetium	0.01–0.9	0.1–0.5	0.2	13
molybdenum	3–100	4 (DL)	---	7
nickel	1–500	14–168	30	24
rubidium	7–100	7–116	12	11
samarium	0.2–5	0.5 (DL)	---	0
scandium	0.06–10	0.1–1.2	0.2	95
selenium	0.1–10	0.8–18	1.9	75
tantalum	0.01–0.28	0.1–0.5	0.1	30
thorium	0.06–1	0.2–1.0	0.3	58
tin	3–90	50–800	125	12
ytterbium	0.04–0.9	0.2 (DL)	---	3
zinc	30–10000	1800 (DL)	---	0

[a] Reference 1–3 and 10. [b] DL = Discrimination Limit.

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Table III. CV Evaluation of Split and Control Samples

element	split coefficient of variation, %	control coefficient of variation, %
antimony	27	26
arsenic	15	15
bromine	12	7
cadmium	31	29
cerium	32	11
chromium	48	13
cobalt	35[a]	8
iron	22	10
lanthanum	35	7
nickel	46	41
scandium	26	6
selenium	24	16
tantalum	32	80
thorium	31	8

[a] After removal of the high outlier value. Without removal, the CV was 244.

of sensitivity of any method to detect the lower concentrations found in the ambient air.

Scan Evaluation. Table II shows that the NAA method as applied to the air particulates on glass-fiber filter samples provided a scan capability for the elements Sb, As, Br, Ca, Cd, Ce, Cr, Cs, Co, Hf, Fe, La, Lu, Mo, Ni, Rb, Sc, Se, Sn, Ta, Th, and Yb.

Repeatability. Table III summarizes the coefficient of variation (CV) for split and control samples (*11*). Only the elements routinely found in the control samples are listed. The CV for split samples indicates the ability of the method to repeat a measurement on any given filter sample; the CV for control samples indicates the ability of the method to repeat measurements on the same sample throughout the period of time needed to perform all composite filter measurements.

The CV is a measure of the consistency of operating parameters indicated by the amount of dispersion around each element mean. A high CV value found in the split samples for cobalt was recalculated with the high outlier removed, and the CV dropped to 35%. Therefore, the split CV analysis for the filter composites demonstrated the repeatability for values initially determined. The high value for the element Ta in the CV analysis of control samples showed that the control data for this element is unsatisfactory. This control material—NBS Coal #1630—did provide the daily checks for half of the elements being scanned.

CONCLUSIONS

The described NAA procedure can analyze for the element arsenic found on glass-fiber filters from samples collected by the NASN programs. Maximum exposure levels for arsenic can be determined by considering those values (23%) above the discrimination limit. While the finite values for arsenic in 85% of the samples (including the 23% above the discrimination limit) are useful in evaluating future trends in the air monitoring programs, the method does provide arsenic values without a need for wet chemistry or the redefining of sampling parameters. The limitations associated with filter material background were overcome by the computer processing of the major γ-ray peak of arsenic in the presence of the interfering bromine and antimony γ-ray peaks and the sodium background contributions. In addition to the arsenic data, the ability to analyze simultaneously information on other elements was demonstrated. The result was the introduction to the NASN data bank of finite concentrations, above the discrimination limits, for 22 of the 26 elements analyzed.

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